Crystal Structure of Poly (2-chloro-p-xylylene) (Special Issue on Polymer Chemistry, XVIII)

AUTHOR(S):

Isoda, Seiji; Ichida, Toshihiko; Kawaguchi, Akiyoshi; Katayama, Ken-ichi

CITATION:

Isoda, Seiji ...[et al]. Crystal Structure of Poly (2-chloro-p-xylylene) (Special Issue on Polymer Chemistry, XVIII). Bulletin of the Institute for Chemical Research, Kyoto University 1983, 61(3): 222-228

ISSUE DATE:

1983-09-20

URL:

http://hdl.handle.net/2433/77037

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 61, No. 3

Crystal Structure of Poly(2-chloro-*p*-xylylene)

Seiji ISODA, Toshihiko ICHIDA, Akiyoshi KAWAGUCHI, and Ken-ichi KATAYAMA*

Received June 8, 1983

The molecular conformation and the crystal structure of poly(2-chloro-*p*-xylylene) were determined by X-ray diffraction. The polymer has a triclinic unit cell with ***a***=5.96 Å, ***b***=12.69 Å, ***c***(fiber axis)=6.66 Å, $\alpha=\gamma=90°$ and $\beta=135.2°$. This unit cell is very similar to that of α-form poly(*p*-xylylene), except the ***b***-axis dimension. Two chains pass through the unit cell and the space group is P1. One monomeric unit makes up the fiber identity period and the internal rotation angles are 0° for the $-CH_2-CH_2-$ bond and 90° for the $-CH_2-\phi-$bond.

The crystallinity of poly(2-chloro-*p*-xylylene) is more easily destroyed by electron bombardment than in the case of poly(*p*-xylylene). The difference in the radiation sensitivity of both polymers is discussed on the basis of their crystal structures. The fact that the polymorphism as in poly(*p*-xylylene) is never observed in poly(2-chloro-*p*-xylylene) can be understood from the structural point of view.

KEY WORDS: Poly(2-chloro-*p*-xylylene)/ Crystal Structure/ Radiation Damage/ Electron Irradiation/ Polymorphism/

INTRODUCTION

Poly(*p*-xylylene), $-(-CH_2-\langle\bigcirc\rangle-CH_2-)_n-$, was found to be strong against electron irradiation[1]. Total end point dose (electron dosage necessary for complete destruction of crystallinity) of this polymer is 0.5 Coulomb/cm^2 at 500 keV and about twenty times larger than that of polyethylene. On the other hand, total end point dose of poly(2-chloro-*p*-xylylene), $-(-CH_2-\langle\overset{Cl}{\bigcirc}\rangle-CH_2-)_n-$, is about 0.05 Coulomb/cm^2. This difference in total end point dose due to substitution of a chlorine for a hydrogen atom depends not only on the molecular structure, but also on the crystal structure. However, the crystal structure of this polymer has not been known and is examined by X-ray diffraction in this article. The relation between the crystal structure and the radiation sensitivity is discussed from the structural result.

When poly(*p*-xylylene) is polymerized at room temperature, its crystal structure is the α-form. On heating, the α-form transforms to the high temperature phase(β_2-form) and melts.[2] However, poly(2-chloro-*p*-xylylene) melts without transforming to any high temperature phase.[3] This difference seems to be deeply connected with the melting mechanism and is discussed from a viewpoint of their crystal structures.

EXPERIMENTAL

Films of poly(2-chloro-*p*-xylylene) were provided by Tomoe Engineering Co., Ltd.

* 磯田正二, 市田俊彦, 河口昭義, 片山健一 : Laboratory of Polymer Crystals, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

Ribons of about $0.4\times2.0\times20.0$ mm size were cut from the film and stretched about six times in an oil bath at 200°C in order to obtain an oriented fiber sample. The X-ray photographs of the stretched sample were taken with CuK_α radiation monochromatized by a graphite crystal, using a cylindrical camera. The stretched sample was doubly oriented so that the ***b***-axis is parallel to the film surface and the ***c***-axis parallel to the stretching direction. This nature of double orientation was used for indexing of the reflections. All reflections were indexed by a triclinic unit cell; $\boldsymbol{a}=5.96$ Å, $\boldsymbol{b}=12.69$ Å, $\boldsymbol{c}=6.66$ Å, $\alpha=\gamma=90°$ and $\beta=135.2°$.

Diffraction intensities were measured on rotation photographs around the fiber axis (Fig. 1). The optical densities of the reflections were measured with a Joyce-Loebl densitometer and transformed to diffraction intensities with a reference density grade. The observed intensity was corrected for Lorentz and polarization factors and for multiplicity. The intensity of a reflection which was not recognizable in the total rotation photograph because of the background from other reflections was measured on the dif fraction photographs taken from the doubly oriented sample fixed at a certain angle. Thirty seven reflections were observed up to the third layer.

Radiation damage measurements were done for crystals of poly(p-xylylene) grown isothermally at 200°C from an α-chloronaphthalene solution and for those of poly(2-chloro-p-xylylene) grown in a slow cooling process in the same solvent. Electron diffraction

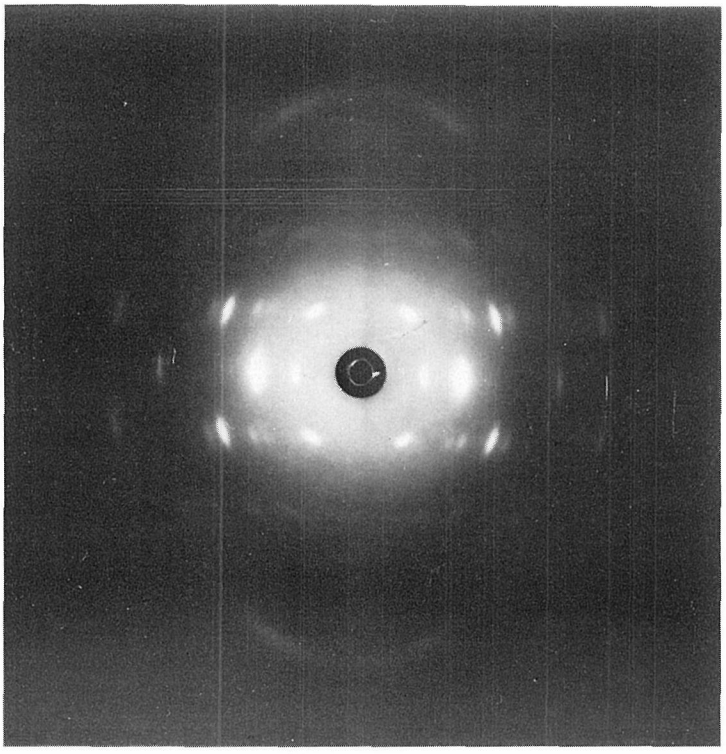

Fig. 1. X-ray diffraction pattern from drawn poly(2-chloro-p-xylylene) taken by the rotating crystal method. The direction of the ***c***-axis coincides with the axis of cylindrical camera and is vertical in this figure.

patterns were taken with 500 keV electron microscope (JEM-500) at regular intervals and the total end point dose was determined by the time necessary for complete destruction of the crystallinity.

STRUCTURE ANALYSIS

X-ray reflections are indexed by the unit cell constants of $\boldsymbol{a}$=5.96 Å, $\boldsymbol{b}$=12.69 Å, $\boldsymbol{c}$=6.66 Å and β=135.2°. The unit cell is similar to that of the α-form poly(*p*-xylylene); $\boldsymbol{a}$=5.92 Å, $\boldsymbol{b}$=10.64 Å, $\boldsymbol{c}$=6.55Å and β=134.7°.[4] This α-form gives a good guidance to analyze the poly(2-chloro-*p*-xylylene) structure. Only the $\boldsymbol{b}$-axis of poly(2-chloro-*p*-xylylene) is longer than that of poly(*p*-xylylene). This suggests that a chlorine atom protruding

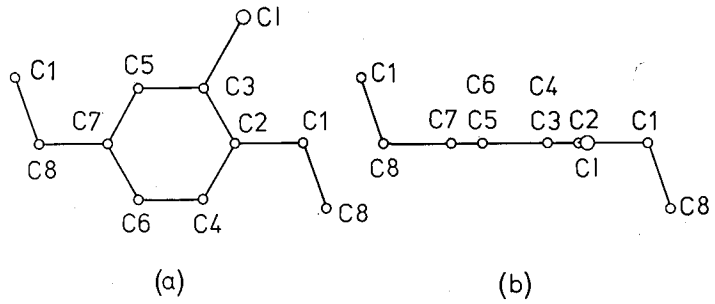

Fig. 2. Two extreme molecular conformations which were considered in the calculation. (a) model 1, (b) model 2

Table I. Observed and calculated structure factors.

h	k	l	F(obs)	F(calc)	h	k	l	F(obs)	F(calc)
0	2	0	16.9	15.5	$\bar{1}$	5	1	6.3	7.6
1	1	0	28.5	26.0	0	6	1	7.2	7.6
0	4	0	9.3	10.9	1	5	1	9.3	6.6
1	3	0	4.3	6.2	$\bar{1}$	7	1	6.7	5.0
1	5	0	3.6	4.4	$\bar{1}$	0	2	3.3	0.3
0	6	0	8.1	5.5	$\bar{1}$	1	2	6.9	8.7
2	0	0	12.2	10.0	$\bar{2}$	0	2	7.8	7.4
2	2	0	2.3	4.2	$\bar{2}$	2	2	7.1	6.5
2	4	0	2.4	3.7	$\bar{1}$	3	2	7.6	6.7
1	7	0	2.5	2.9	0	0	2	7.9	6.5
0	8	0	1.8	2.3	0	2	2	6.3	5.6
3	3	0	1.3	1.9	$\bar{2}$	4	2	6.4	7.7
$\bar{1}$	1	1	14.5	16.0	$\bar{1}$	5	2	6.9	6.4
0	0	1	9.2	11.5	$\bar{3}$	3	2	4.6	3.9
0	2	1	9.1	10.3	$\bar{2}$	6	2	4.7	4.8
$\bar{1}$	3	1	11.2	10.8	0	6	2	4.2	2.9
$\bar{2}$	0	1	18.7	20.6	$\bar{2}$	2	3	6.8	5.0
0	4	1	10.6	11.7	$\bar{2}$	4	3	3.1	4.4
$\bar{2}$	2	1	7.9	6.4					

from a benzene ring aligns nearly parallel to the ***b***-axis in the case of poly(2-chloro-*p*-xylylene).

Since no systematic absence is observed, the resonable space group is P1. Two extreme molecular conformations shown in Fig. 2 (a) and (b) correspond to those of

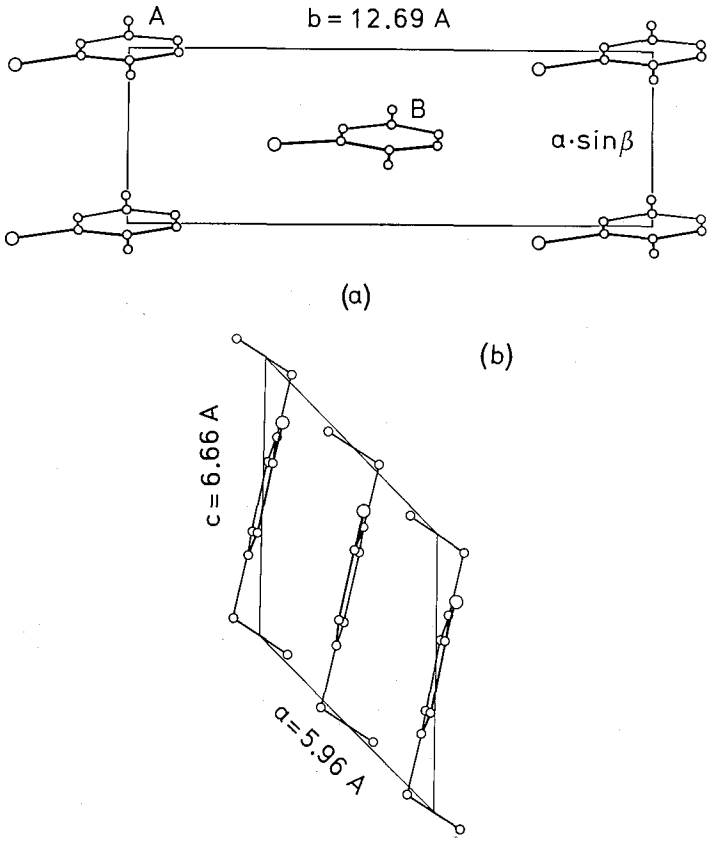

Fig. 3. Crystal structure of poly(2-chloro-*p*-xylylene). (a) Projection on the plane perpendicular to the ***c***-axis, (b) Projection on the ***ac***-plane. ∘ carbon ; ○ chlorine.

Table II. Refined fractional coordinates of atoms. A and B molecules are represented in Fig. 3 (a).

molecule	atom	u	v	w
A	C1	0.1547	0.0018	1.0269
	C2	0.0738	0.0008	0.7518
	C3	0.0457	−0.0921	0.6319
	C1	0.1006	−0.2030	0.7888
B	C1	0.6547	0.4982	1.0269
	C2	0.5738	0.4992	0.7518
	C3	0.5257	0.4071	0.6192
	C1	0.5567	0.2953	0.7609

$\theta=0°$ (model 1) and $\theta=90°$ (model 2), where θ is the internal rotation angle for $-CH_2-\phi-$ bond. In the least squares calculation, intermediate values of θ were also considered. Parameters for the least squares method are the fractional coordinates of three carbon and one chlorine atoms (C1, C2, C3, Cl in Fig. 2). Hydrogen atoms were not included in the calculation. By qualitative comparison of the calculated and observed structure factors, the molecular model having the conformation of model 2 was chosen. The chain conformation of model 2 is similar to that of poly(*p*-xylylene). The crystal structure shown in Fig. 3 was finally obtained. The observed and calculated structure factors are compared in Table I. Up to the third layer line, the R factor ($R=\Sigma||F(obs)|-|F(calc)||/\Sigma|F(obs)|$) is 17%, which indicates the crystal structure is reasonable. Atomic coordinates are given in Table II. The temperature factor is about 10 Å^2 and is somewhat higher than the factors of other polymers. This may be caused by disorders in the crysral due to chemical irregularity, *i.e.,* the head-to-head or tail-to-tail polymerization. This speculation is supported by the fact that the amorphous halo in Fig. 1 is stronger than that of poly(*p*-xylylene), *i.e.,* the crystallinity is lower because of the chemical irregularity.

DISCUSSION

In the obtained molecular conformation of poly(2-chloro-*p*-xylylene), the internal rotation angle is 0° (trans) for the $-CH_2-CH_2-$ bond, while it is 90° for the $-CH_2-\phi-$ bond. These angles are the same as in to the *α*-form of poly(*p*-xylylene). In the molecular arrangement of the crystal structure, the benzene ring in A molecule makes an angle of 2° with the ***b***-axis, and that in B molecule an angle of −2° (see Fig. 3 (a)). The ***b***-axis of poly(2-chloro*p*-xylylene) is longer than that of poly(*p*-xylylene) due to the protruding chlorine atom.

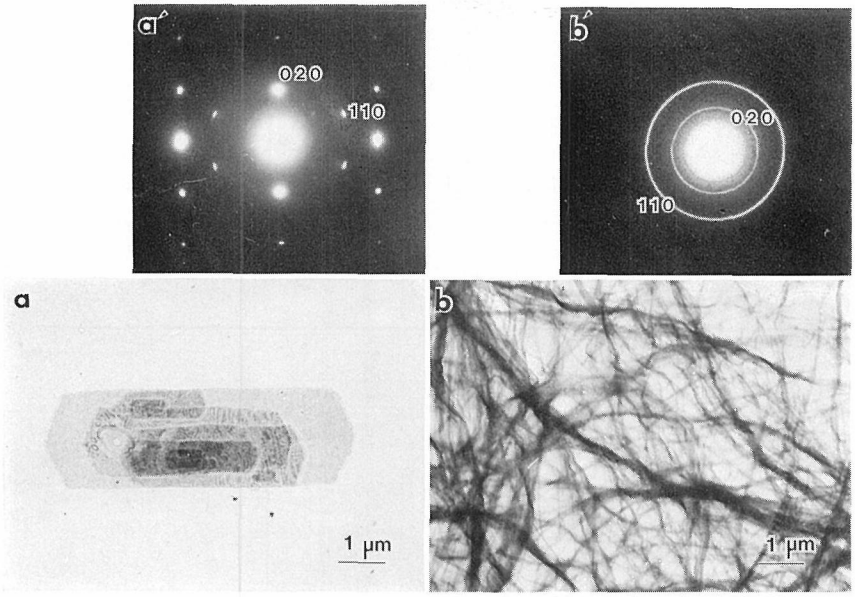

Fig. 4. (a) Solution grown crystal of *α*-form poly(*p*-xylylene), (b) of poly(2-chloro-*p*-xylylene). (a′) and (b′) are electron diffraction patterns from respective crystals.

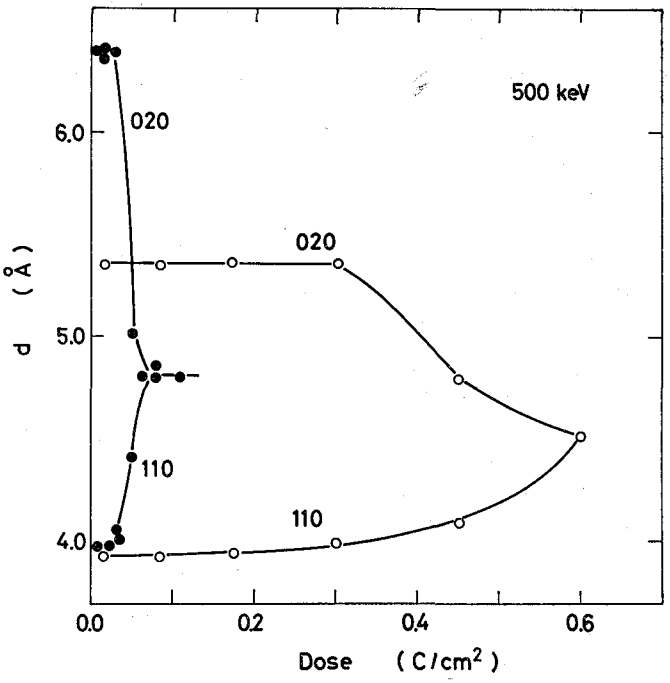

Fig. 5. Changes of the lattice spacings of poly(*p*-xylylene), ○, and poly(2-chloro-*p*-xylylene), ●, due to 500 keV electron irradiation.

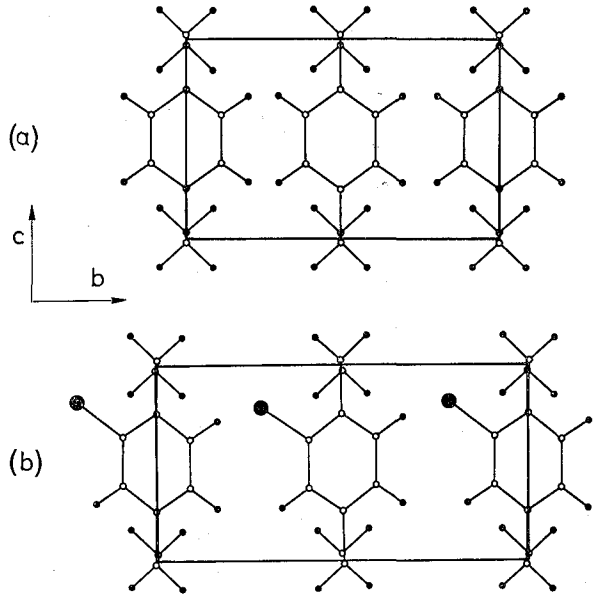

Fig. 6. Projections on the ***bc***-plane of poly(*p*-xylylene) (a), of poly(2-chloro-*p*-xylylene) (b). • hydrogen; ○ carbon; ● chlorine.

The α- and β-forms are known for poly(p-xylylene)[5]. By annealing above 250°C, the α-form transforms to the β-form where the molecules distribute statistically.[6] At high temperatures, the rotation of chains is largely excited and lattice distortions are induced in the poly(p-xylylene) crystal, resulting in the crystal transformation.[3] Poly (2-chloro-p-xylylene), however, never changes to distorted phases by heat treatment. If the rotation of chains took place thermally in poly(2-chloro-p-xylylene), this motion of chains with protruding chlorine atoms would severely affect the positions of the nearest molecules and the large fluctuation of the relative positions would cause the melting without transforming to the high temperature phase as in poly(p-xylylene).

Figure 4 (a) and (b) show the solution grown crystals of poly(p-xylylene) and poly(2-chloro-p-xylylene). Their electron diffraction patterns (a′) and (b′) show that poly(p-xylylene) is crystallized as a single crystal and poly(2-chloro-p-xylylene) as a aggregate of fibers. Figure 6 shows the lattice spacing changes of α-form poly(p-xylylene) and poly (2-chloro-p-xylylene) crystals due to 500 keV electron bombardment. Both polymer crystals were destroyed completely by electron irradiation equivalent to respective total end point doses; 0.5 for poly(p-xylylene) and 0.05 Coulomb/cm^2 for poly(2-chloro-p-xylylene). The process of radiation damage can be considered as follows; After a C-H bond scission due to electron bombardment, the hydrogen diffuses and is released from crystal surface.[7] In poly(2-chloro-p-xylylene) hydrogen atoms or molecules can diffuse more easily than in poly(p-xylylene) because of the larger unit cell (see Fig. 6).

In data analysis the FACOM M-180 II AD at the computer center of the Institute for Chemical Research, Kyoto University, was used.

REFERENCES

(1) M. Tsuji, S. Isoda, M. Ohara, A. Kawaguchi, and K. Katayama, *Polymer*, **23**, 1568 (1982).
(2) W. D. Niegisch, *J. Appl. Phys.*, **37**, 4041 (1966).
(3) S. Isoda, A. Kawaguchi, and K. Katayama, Submitted for publication in *J. Polym. Sci., Polym. Phys.*
(4) R. Iwamoto and B. Wunderlich, *J. Polym. Sci., Polym. Phys.*, **11**, 2403 (1973).
(5) C. J. Brown and A. C. Farthing, *J. Chem. Soc.*, **1953**, 3270 (1953).
(6) S. Isoda, M. Tsuji, M. Ohara, A. Kawaguchi, and K. Katayama, *Polymer*, in press.
(7) T. Kobayashi, H. Kurata, and N. Uyeda, *10th International Congress on Electron Microscopy*, **2**, 461 (1982).